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## A NOTE ON THE ADSORPTION OF HYDROGEN ON REDUCED NICKEL.

By SHUN-ICHIRO IJIMA.

A series of studies on the adsorption of hydrogen on reduced nickel have been made by the author. Some of these studies have already been published<sup>1)</sup> and yet there remain some other interesting subjects, which will be taken up here as a supplementary note.

### Experimental.

#### Materials, Apparatus and Experimental Method.

The materials, the apparatus and the experimental method are the same as in the reports already published.

Nickel used was prepared from about 10 g. of nickel oxide. In the experiments on adsorption velocity, unless specially mentioned, the pressure was about 23.5 cm. 1 minute after the start.

### Experimental Results and their Consideration.

#### Irreversibility of Adsorption and Desorption.

Let  $a$  and  $a'$  represent the adsorbed amounts respectively in the following two cases: (1) desorbed reduced nickel kept at a temperature of  $t_1$  being sealed together with a given amount of hydrogen, an equilibrium is established and (2) the same system being kept at a temperature of  $t_2$  higher than  $t_1$  for some time and then once more at  $t_1$ , and equilibrium is established. Then there holds the following relation:

$$a < a'.$$

In Figs. 1 and 2, (i) shows the process of the adsorption at a temperature of  $t_1$ , (ii) that at a changed temperature,  $t_2$ , and (iii) that again at the former temperature. These show evidently the relation,  $a < a'$ .

Such a relation, however, never holds in the case of the adsorption of nitrogen on reduced nickel<sup>2)</sup>, that is,  $a = a'$  independent of such a change of temperature.

Again, in these figures, (iv) shows the process of the adsorption at a further changed temperature, i. e., once more at the temperature of (ii),  $t_2$ . The adsorbed

1) Iijima, This Journal, 7, 3, 24, 36 (1933); 12, 1, 148 (1938); 13, 1 (1939).

2) Iijima, This Journal, 13, 42 (1939).

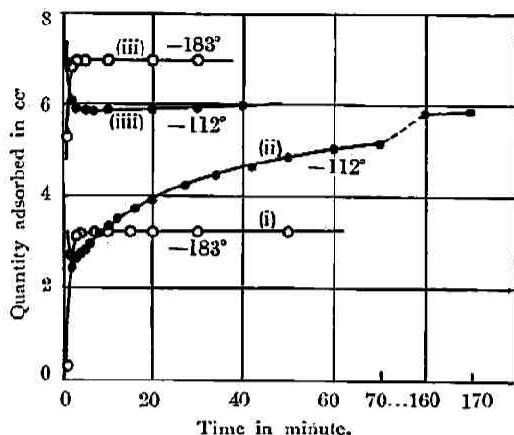


Fig. 1

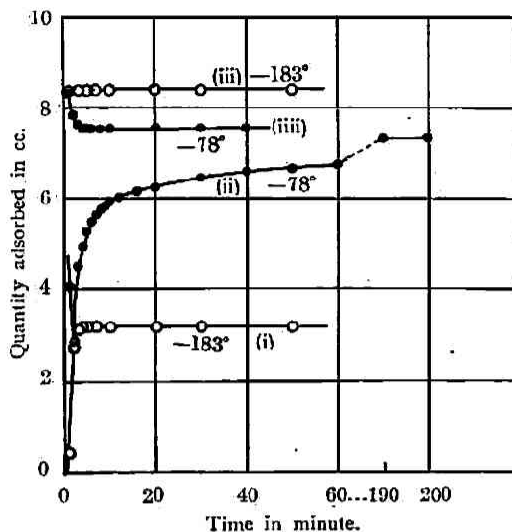


Fig. 2

amounts in the two cases, (ii) and (iv), are nearly equal. And this indicates that the adsorbed amount is unchangeable though the temperature of the system which has reached an equilibrium at  $t_2$  is lowered to  $t_1$  and once more restored to  $t_2$ . It is the same with the case of nitrogen.

#### Desorption at Low Temperatures.

However long the hydrogen adsorbed on reduced nickel at  $-112^\circ$ ,  $-78^\circ$ ,  $+20^\circ\text{C}$ . etc. is evacuated at respective temperatures, only a small part of it can be desorbed. This is evidently ascertained by a comparison of the adsorption velocity in the case when hydrogen is adsorbed on the reduced nickel at a low temperature and evacuated at the same temperature for a long time with that in the case when hydrogen is adsorbed on the reduced nickel and then completely desorbed by evacuation at high temperatures. In Fig. 3, (i) shows the adsorption process on the nickel presumed to have been thoroughly desorbed by the evacuation at  $280^\circ\text{C}$ . after the adsorption at  $-112^\circ\text{C}$ ., and (ii) shows the process of the adsorption following many hours' evacuation at  $-112^\circ\text{C}$ . after the adsorption at the same temperature. Discrepancy

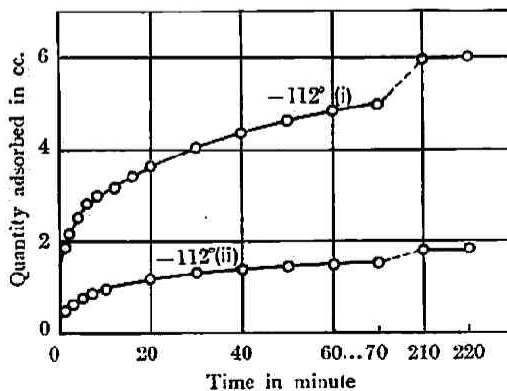


Fig. 3

between these two curves indicates that part of hydrogen adsorbed by reduced nickel is hard to be desorbed by evacuation at low temperatures.

It is, however, generally possible for nitrogen adsorbed by reduced nickel<sup>19</sup> to be desorbed completely by evacuation at the same temperature as it was adsorbed. So far as this point is concerned, there is a noticeable difference between the adsorption of hydrogen and that of nitrogen.

#### The Relation between the Temperature of Reduction and the Adsorbed Amount.

Using the nickel which had been reduced at 280°C., the adsorbed amounts of hydrogen at 20° and -183°C. were measured. Then, hydrogen was passed on the same nickel while being heated to 290°C. and the adsorbed amounts were measured at the same temperatures 20° and -183°C. Thereafter, every time hydrogen was passed at higher temperatures, a similar measurement was carried out. The results obtained are given in Tables I and II. Table I is the case when hydrogen was passed for 1~2 hours at high temperatures, and Table II the case when it was passed for 2~5 hours.

The values of Tables I and II are graphically shown in Fig. 4. From the figure it is seen that the amount adsorbed at 20°C. by the nickel reduced at

Table I

Reduced nickel...Prepared from 10.1129g. of nickel oxide.

Reduction...17 c.c. of Hydrogen passed every one minute (1 liter every hour).

Reduction				Adsorbed amount (c.c. N.T.P.)	
Temperature C.	Time (hour)	Quantity of water		20°C.*	-183°C.**
		Weight (g.)	Percentage of the theoretical value		
280	67.5	2.3550	90.64%	14.23	3.40
290	1	0.0119	} 3.10%	13.37	3.75
300	2	0.0184		11.82	3.70
310	1	0.0067		11.29	3.87
320	1	0.0053		10.28	4.15
330	1	0.0030		9.65	3.97
340	1	0.0061		9.07	—
350	1	0.0010		8.67	3.85
360	1	0.0054		8.30	3.82
460	1	0.0179		5.99	2.03
Total		2.4307	99.64%		

\* Total adsorbed amount after 18 hours from the beginning. Pressure of hydrogen was  $23.36 \pm 0.03$  cm. one minute after the start.

\*\* Total adsorbed amount under the equilibrium pressure of  $18.52 \pm 0.07$  cm.

Table II

Reduced nickel.....Prepared from 10.0516 g. of nickel oxide.  
Rate of reduction...The same as in Table I

Reduction		Adsorbed amount (c.c. N.T.P.)	
Temperature	Time (hour)	20°C.*	-183°C.**
280 C°.	60	14.71	3.01
290	5	12.27	3.43
300	5	10.97	4.40
310	5	6.94	5.02
320	5	9.22	5.27
330	2	8.81	4.68
340	2	8.58	4.55
360	2	8.05	4.25
460	2	4.74	2.61

\*, \*\* See corresponding note in Table I.

280°C. is larger than that adsorbed at -183°C. Nevertheless, continued high temperature treatments lead to an abrupt decrease in the amount adsorbed at 20°C., but a gradual decrease at -183°C. Accordingly, generally speaking, the higher the temperature of treatment is, the more the adsorbed amount of both cases approximate to each other. It seems probable that more higher temperature treatment makes the amount adsorbed at 20°C. less than that at -183°C.

These facts show that high temperature treatment has hardly any influence upon the amount of the van der Waals adsorption, though much

upon the activated adsorption amount. The cause of such phenomena is ascribable to the destruction of active centres due to high temperature treatment.

What, then, brings forth the destruction of active centres? As the factors, the following will be considered:

- (1) Sintering of nickel caused by high temperatures.
- (2) Poisoning at high temperatures by a trace of another gas contained in

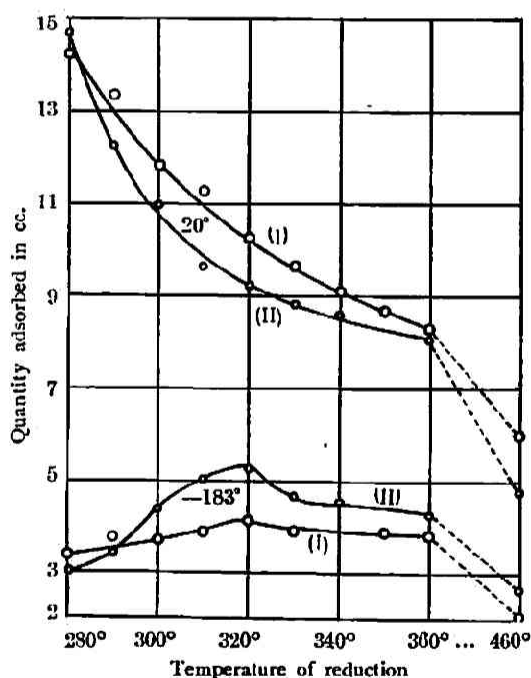


Fig. 4

hydrogen used for reduction.

(3) Physical action between the active centres and the hydrogen molecules. Of these three, (i) will be the determining factor.

The amount adsorbed at  $-183^{\circ}\text{C}$ . shows a tendency to increase at first by continued high temperature treatment. This can not be ascribed to the enlargement of the nickel surface due to the approach to the completion of reduction, as seen from a comparison between the water formed by high temperature treatment and the adsorbed amount (Table I). This phenomenon can be explained assuming that there are gaps on the nickel surface<sup>3)-5)</sup>, but here this question will not be touched upon.

#### Reduction Temperature and Completion of Reduction.

It has been generally admitted that reduced nickel is prepared by the reduction of nickel oxide which is produced by the decomposition of nickel nitrate at about  $300^{\circ}\text{C}$ ., and the time when water vapour almost ceases to come out shows the completion of reduction. That such a treatment as this is, strictly speaking, insufficient for the completion of reduction is evident from the column 'reduction' of Table I. In Table I, 'theoretical value' indicates the amount of the water to be formed in the case when the composition of nickel oxide is taken as  $\text{NiO}$ . And in fact, that the total amount of the water formed was 99.64% of the theoretical value indicates that the composition of nickel oxide prepared by decomposition of nickel heated to about  $300^{\circ}\text{C}$ . is  $\text{NiO}$ .

#### Shift of the Maximum and the Minimum Points on Adsorption Isobar.

There are not a few adsorption systems whose isobar have either a maximum point, a minimum one, or both<sup>6)</sup>. No paper seems, however, to have been published on the shift of the maximum and the minimum points on it.

(1) Shift by the difference of the reduction temperature.

It is supposed that there are various active centres with different degree of activity on the surface of reduced nickel. In case reduced nickel reduces its own activity, the active centres of high activity will disappear at a higher rate than those of less activity because of (1) ready transition to less active centres, (2) exhaustion of activity, etc. Accordingly, in the reduced nickel which has

3) Howard, *Trans. Farad. Soc.*, **28**, 399 (1932).

4) Patrick, *J. Phys. Chem.*, **41**, 437 (1937).

5) Ganguli, *Kolloid-Z.*, **71**, 275 (1935).

6) Fischbeck etc., *Z. physik. Chem.*, **A**, **171**, 385 (1935); Lewis and Taylor, *J. Am. Chem. Soc.*, **60**, 877 (1938).

reduced its own activity the active centres are not only small in number, but also low in the mean activity. And the higher in activity the centres are the more readily they can make an activated adsorption at low temperatures. It follows, therefore, that reduced nickel with high activity makes an activated adsorption at lower temperature than that with low activity.

As already mentioned above, high temperature reduction markedly lessens an activated adsorption, but quite slightly the van der Waals adsorption. The appearance of the maximum and the minimum points on the adsorption isobar are ascribed to a quantitative relation between two kinds of adsorption.<sup>7)</sup> Therefore, with the rise of reduction temperature they should shift to the high temperature side. For example, in the case of the adsorption of hydrogen on the nickel reduced at 400°C. the minimum point appears at about -90°C. under 20 cm. pressure<sup>8)</sup>, while in the nickel reduced at 280°C., it does at a far lower temperature—about -150°C. (See Fig. 5) Fig. 5 gives the curve drawn from the approximate values of the adsorbed amount at the time an equilibrium has been established, which were obtained by the extrapolation of the adsorption velocity curve<sup>9)</sup>, and from the value directly obtained (the adsorption at -183°C.; cf. Fig. 4). This figure is not accurate, as the pressure of one adsorption is different from that of another, but it may give an outline of the tendency.

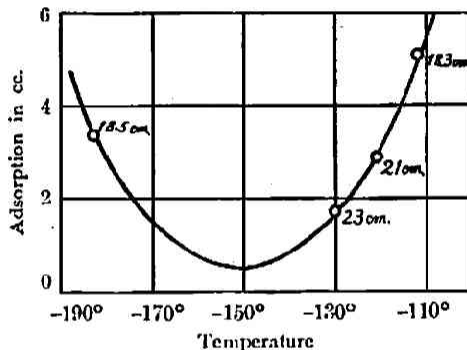


Fig. 5

## (2) Shift by the change of pressure.

The relation between the adsorbed amount and the equilibrium pressure should vary in each activated adsorption or the van der Waals adsorption. Hence, the maximum and the minimum on adsorption isobar must shift according to the change of equilibrium pressure.

### The Adsorption at -183°C.

The results were obtained which seem to make it difficult to judge whether the adsorption of hydrogen by reduced nickel at -183°C. includes an activated adsorption or not, that is,

- (1) It is difficult for the hydrogen adsorbed on reduced nickel to be desorbed

7) Taylor, *J. Am. Chem. Soc.*, **53**, 578 (1931).

8) Iijima, *This Journal*, **7**, 32 (1933), Fig. 7.

9) Iijima, *ibid.*, **12**, 5 (1938), Fig. 4.

thoroughly by evacuation at the same temperature  $-183^{\circ}\text{C}$ . This can be ascertained by a comparison of the adsorbed amount obtained after such an evacuation with that obtained after the evacuation at higher temperature ( $280^{\circ}\text{C}$ .) The results are given in Table III.

Table III

Reduced nickel.....Prepared from 10.0273 g. of nickel oxide.

Evacuation.....2 hours after becoming "vacuum",

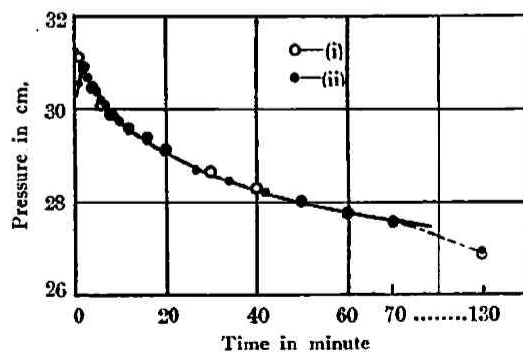
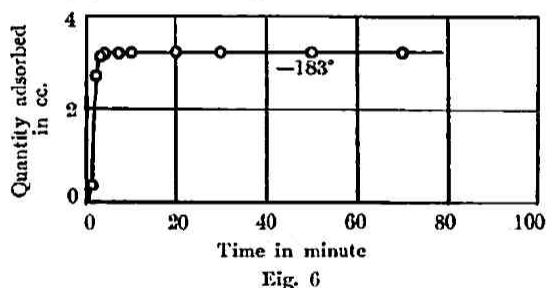
Adsorption follow a evacuation at high temperature			Adsorption follow a evacuation at $-183^{\circ}\text{C}$ .			Difference of the adsorbed amount
Temperature	Pressure	Adsorbed amount	Temperature	Pressure	Adsorbed amount	
$-183^{\circ}\text{C}$ .	20.76 cm	2.76 c.c.	$-183^{\circ}\text{C}$ .	20.76 cm.	1.56 c.c.	1.20 c.c
"	23.42	2.87	"	23.42	1.66	1.21

Supposing that adsorption which has been left undesorbed by evacuation at  $-183^{\circ}\text{C}$ . is the activated adsorption, about 45% of the whole adsorption will be activated adsorption.

(2) The adsorption velocity curve at  $-183^{\circ}\text{C}$ . (Fig. 6) assumes a shape markedly different from any other adsorption velocity curves at low temperatures<sup>10)</sup>. The adsorption hardly proceeds 2~3 minutes after the start. Such is the case with the velocity curve of a small amount of the activated adsorption, such as the

adsorption by the reduced nickel either sintered by high temperature treatment or regarded as saturated for the activated adsorption. This indicates that the amount of the activated adsorption at  $-183^{\circ}\text{C}$ . is either extremely small or zero.

(3) The adsorption velocity curve in the case when the temperature of the system—reduced nickel and hydrogen which has reached



10) Iijima, This Journal, 12, 1 (1938).



equilibrium at  $-183^{\circ}\text{C}.$ —is quickly changed to  $-112^{\circ}\text{C}.$  (Fig. 7\* (ii)) is of a type similar to the adsorption made at  $-112^{\circ}\text{C}.$  from the beginning, (Fig. 7 (i)) and the velocity constants in both cases are nearly equal, as shown in Table IV.

Table IV

Reduced nickel.....Prepared from 10.0273 g. of nickel oxide.

Adsorption	Velocity constant of adsorption ( $k_1$ ) $\times 10^6$
Fig. 7 (i)	0.113
Fig. 7 (ii)	0.111

The experimental results described in (1) and in (2) and (3) which may seem contradictory will be understood as follows.

At  $-183^{\circ}\text{C}.$  the velocity constant of desorption is remarkably small as compared with that of adsorption. Consequently, even under such an extremely low pressure as to be regarded as vacuum, the adsorbed amount of hydrogen is considerably large. This can be understood by the fact that the isothermal line is included in the abscissa<sup>11)</sup>—adsorbed amount axis—until the adsorption amount becomes moderately large. Any ordinary evacuation at low temperature is inadequate for complete vacuum, and so even the van der Waals adsorption can not be desorbed thoroughly.

In short, from the evidences mentioned in (2) and (3) it may be concluded that the whole or almost the whole adsorption of hydrogen at  $-183^{\circ}\text{C}.$  is the van der Waals adsorption, so far as reduced nickel is concerned.

### Summary.

- 1) Both the adsorption and desorption of the system consisting only of hydrogen and reduced nickel under the change of temperature is irreversible.
- 2) It is difficult for hydrogen adsorbed by reduced nickel to be desorbed by evacuation at low temperatures.
- 3) If the reduction temperature is raised in the preparation of reduced nickel, the amount of activated adsorption on it remarkably decreases, while that of the van der Waals adsorption slightly does as compared with the former.
- 4) Strictly speaking, it is difficult for us to obtain nickel which has been completely reduced by the reduction at  $280^{\circ}\text{C}.$

\*) The curve of adsorption velocity is, for convenience, represented by the graph showing the relation between the time and pressure.

11) Iijima, This Journal, 7, 24 (1933); *Sc. Pap. I. P. C. R.* 23, 34 (1933).

5) The maximum and the minimum points on the adsorption isobar should shift according to the activity of reduced nickel and the pressure of a gas.

6) The whole or almost the whole of hydrogen adsorbed by reduced nickel at  $-183^{\circ}\text{C}$ . is the van der Waals adsorption.

The author wishes to express his appreciation to Prof. S. Horiba for his kind guidance throughout this work.

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